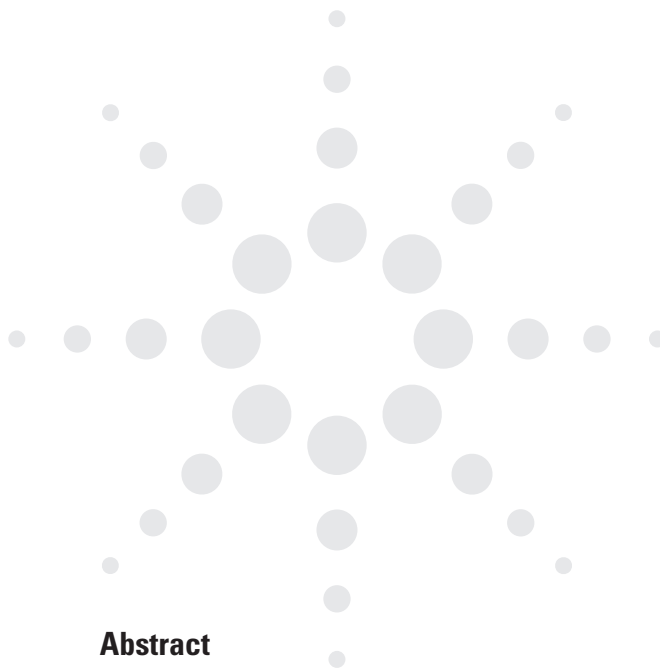


# Using the ICP-MS as a Rapid Survey Tool for Semiquantitative Analysis

## Application Note

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### Abstract

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) provides users with simple spectra that can be used to qualitatively investigate unknown samples. The simple spectra also allow approximate concentrations to be calculated, “semiquantitatively”. In order for this data to be useful, the ICP-MS instrument software must provide a simple way to convert the raw spectrum into concentration data. The instrument itself must also provide rapid analysis, sufficient signal to noise to allow quantification for elements at low concentration and a wide dynamic range so that excessive sample dilution is not required.

The 4500 ICP-MS, combined with the powerful ChemStation software, meets all of the requirements for the provision of semiquantitative analysis, as illustrated within this note. Several environmental reference materials were investigated using this rapid survey analysis method and the data illustrates values within +/- 20% of the expected with, essentially, no calibration.



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## Introduction

One of the well-documented benefits of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the simplicity of the spectra obtained. These spectra are easy to interpret and are frequently used to “fingerprint” unknown samples, using the relative intensities of the various elements observed. Such spectra can also provide a means of generating approximate concentrations for un-calibrated elements in a sample. This quantification can be done by comparing the unknown elements to an element (or elements) of known concentration, either in a reference sample or in the unknown sample itself. In ICP-MS this approach is called semiquantitative analysis and is frequently used for rapidly surveying unknown materials and samples.

Semiquantitative analysis is useful in situations where calibration standards are unavailable, as is often the case, for example, with solids analysis by laser ablation.

The 4500 ICP-MS possesses the four important analytical criteria for good survey analysis:

- high speed of analysis, which provides high sample throughput
- excellent signal to noise, providing users with good quantification of elements at low concentration
- wide dynamic range, which avoids the need for sample dilution and re-running
- a flat response curve, which means that sensitivity is not highly dependent on mass

## What is Semiquantitative Analysis?

Unknown samples are typically spiked with a known amount of an internal standard prior to analysis. The elemental intensities measured are compared with the intensity of the internal standard spike, giving a relative concentration result.

Ideally, an ICP-MS should give acceptable semiquantitative results, regardless of the mass of the analyte and the complexity of the sample matrix. These criteria are affected by two fundamental ICP-MS parameters:

### \* Mass bias (or mass response)

### \* Efficiency of ionisation

#### Mass bias (or mass response)

In common with all other mass spectrometers, the 4500 ICP-MS does not transmit exactly equal amounts of all elements introduced. The relative transmission at different mass regions is known as “mass bias”. The result is that the signal for a given concentration of any element will depend on its mass. This mass bias or mass response is small on the 4500 ICP-MS and can be easily

“mapped” with a simple multi-element standard (figure 1).

A high degree of mass bias could compromise the accuracy of semiquantitative analysis, as the analyte may be widely separated from the reference element. Stability of the mass response is also an important factor. Both of these factors are affected by the design of the ion optics of the instrument.

ICP-MS instruments require electrostatic lenses to focus the ions, and to separate them from the photons and neutral species introduced as part of sampling. Older designs of instruments used a centrally mounted disc as part of the ion focussing system. This design requires the ions to be defocussed before the disc and then refocussed after the disc. Both of these actions are inefficient and inevitably introduce mass bias as the degree of defocussing is mass dependent. In the 4500 ICP-MS, in contrast, the ions are kept in a compact, collimated beam at all times, and are deflected off axis by a low voltage ion lens just before the quadrupole (figure 2). This configuration introduces minimal mass bias.

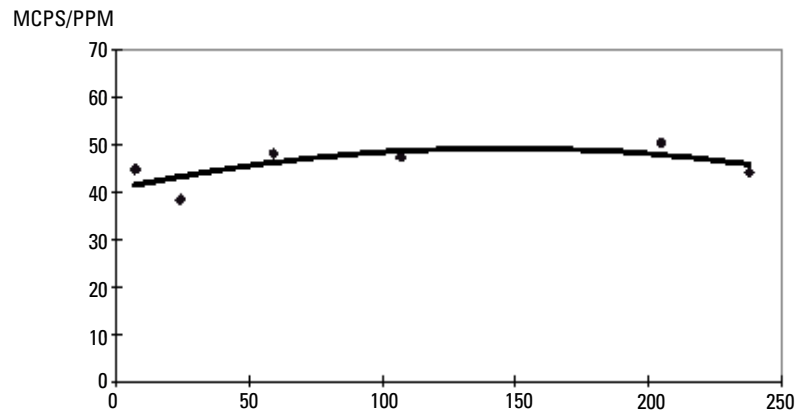
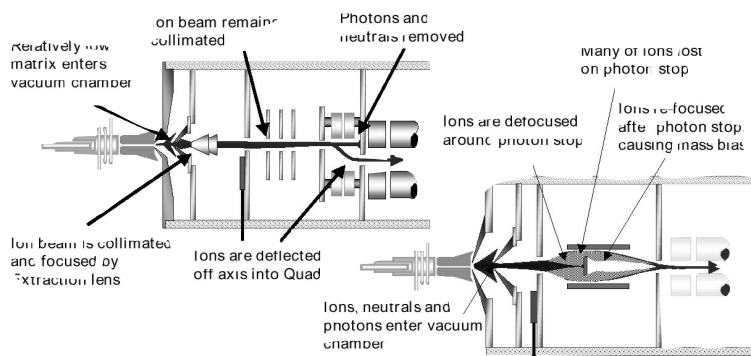
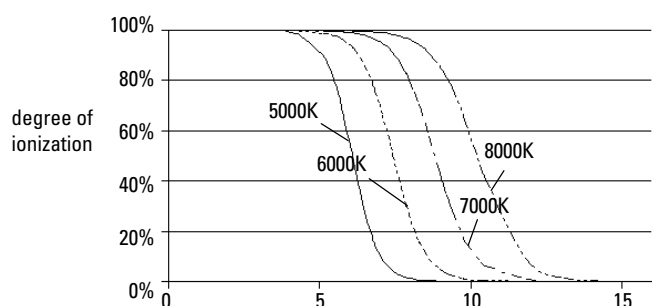


Figure 1.  
Typical response curve of a 4500 ICP-MS



**Figure 2.**  
**Off axis and neutral stop lens systems**



**Figure 3**  
**Effect of plasma temperature on ionization**

$$\frac{N_{ij}}{N_{aj}} = \frac{(2\pi m_e kT)^{3/2} 2z_{ij}}{N_e h^3 z_{aj}} e^{-e_j/kT}$$

**Equation 1**

where

- $N_{ij}$  is the ion conc of species j
- $N_{aj}$  is the atom concentration of species j
- $N_e$  is the free electron concentration
- $m_e$  is electron mass
- $k$  is Boltzmann's constant
- $h$  is Planck's constant
- $z_{ij}$  is the partition function of ions j
- $z_{aj}$  is the partition function of atoms j
- $e_j$  is the ionisation potential of species j
- $T$  is the ionisation temperature

#### Efficiency of ionisation

The population of single charged species available in the plasma will differ according to the ionisation potential of the element. The percentage of singly charged ions formed from atoms introduced to the plasma can be predicted with reasonable accuracy using the Saha equation (Equation 1).

Figure 3 illustrates how the population of singly charged species changes with plasma temperature. It is important to have a high temperature ionisation source for ICP-MS, to ensure low oxide interferences and a high

proportion of singly charged ion species. The 27.12 MHz argon plasma is the first choice for ICP-MS and ensures that every element with an ionisation potential below 7.5 eV will be essentially 100% ionised.

Obviously, the smaller the correction factors required for the less well ionised elements, the better and more accurate the data.

The high temperatures and relatively high electron densities of the ICP operating at 27.12MHz mean that consistent high ionisation is achieved, even on complex samples. This ensures that the Saha correction factors are appropriate for most elements in a wide range of sample types.

For effective semiquantitative analysis, the acquired data must be:

1. corrected for any mass bias
2. normalized for the abundance of the isotope measured
3. corrected for the degree of ionisation of the element in the plasma.

The 4500 ICP-MS ChemStation software automates the complete calculation process, providing a fast multi-element analytical method for screening.

#### Analytical data

Table 1 summarizes a typical semiquantitative analysis from a sample of SLRS-3 River water. The data was obtained by spiking the acidified sample with 10 ppb of Y, aspirating the spiked sample into the instrument, and acquiring data over the complete mass range, a process which took approximately 60 seconds.

element	mass	found	certified	unit
Li	7	710		ng/l
Be	9	<14.00	5	ng/l
B	11	7.8		µg/l
Na	23	1.8	1.6	mg/l
Mg	24	1	1.6	mg/l
Al	27	24	31	µg/l
Si	29	1.1		mg/l
K	39	330	700	µg/l
Ca	43	3.1	6	mg/l
Sc	45	110		ng/l
Ti	47	570		ng/l
V	51	300	300	ng/l
Cr	53	330	300	ng/l
Mn	55	3.4	3.9	µg/l
Fe	57	99	100	µg/l
Co	59	27	27	ng/l
Ni	60	790	830	ng/l
Cu	63	1.2	1.35	µg/l
Zn	66	1	1.04	µg/l
Ga	69	1.3		µg/l
Ge	72	66		ng/l
As	75	620	720	ng/l
Se	82	530		ng/l
Br	79	23		µg/l

element	mass	found	certified	unit
Rb	85	1.7		µg/l
Sr	88	32	28	µg/l
Y	89	Internal Standard		ng/l
Zr	90	100		ng/l
Nb	93	5.7		ng/l
Mo	95	310	190	ng/l
Tc	99	<1.700		ng/l
Ru	101	<8.500		ng/l
Rh	103	<1.700		ng/l
Pd	105	8.4		ng/l
Ag	107	<3.500		ng/l
Cd	111	27	13	ng/l
In	115	1.9		ng/l
Sn	118	12		ng/l
Sb	121	120		ng/l
Te	125	<94.00		ng/l
I	127	24		µg/l
Cs	133	10		ng/l
Ba	137	13		µg/l
La	139	330		ng/l
Ce	140	410		ng/l
Pr	141	70		ng/l
Nd	146	290		ng/l
Sm	147	70		ng/l

element	mass	found	certified	unit
Eu	153	11		ng/l
Gd	157	50		ng/l
Tb	159	5.3		ng/l
Dy	163	27		ng/l
Ho	165	5.4		ng/l
Er	166	20		ng/l
Tm	169	<2.000		ng/l
Yb	172	13		ng/l
Lu	175	2.5		ng/l
Hf	178	2.4		ng/l
Ta	181	<2.100		ng/l
W	182	<9.400		ng/l
Re	185	<6.000		ng/l
Os	189	<56.00		ng/l
Ir	193	<2.700		ng/l
Pt	195	<9.000		ng/l
Au	197	<3.800		ng/l
Hg	202	51		ng/l
Tl	205	11		ng/l
Pb	208	63	68	ng/l
Bi	209	3.3		ng/l
Th	232	24		ng/l
U	238	39	45	ng/l

**Table 1**  
- Semiquantitative analysis of SLRS- 3 River water standard

As the data in Table 1 illustrates, there is generally good agreement for the certified concentrations in the river water standard from the sub ppb level (Pb, U) to ppm (Na, Mg). This is especially impressive for such a rapid analysis, given that the analyte concentrations were calculated from only a single internal standard spike. The semiquantitative routine provides a rapid and relatively accurate means of surveying unknowns over a wide dynamic range.

#### Analysis of Soil Digest

IAEA Soil 7 is a well-characterised soil standard. 250 mg of this standard was acid digested and the dissolved material made up to 100mLs in 1% nitric acid. This solution was spiked with 10 ppb of Y as an internal standard. As

with the river water standard, the 4500 ICP-MS was used in scan mode to gather data across the complete mass range.

Table 2 summarises the semiquantitative results for the Soil 7 standard material. The data has been corrected for the dilution factor (x400) and expressed in the appropriate units. The certified values are also included in the table, for comparison. As with the previous example, the semiquantitative values for these analyses agree well with the certified concentrations. Good agreement was obtained for a wide range of elements over a wide dynamic range, despite the short acquisition time and the large multiplication factor associated with the dilution.

## Conclusion

ICP-MS offers several advantages over other techniques for inorganic analysis in terms of wide element coverage, low detection limits and rapid sample throughput. The stable and flat mass response of the 4500 ICP-MS means that good quantification can be obtained by referencing unknown elements to a single internal standard. The powerful ChemStation software provides semiquantitative data from rapid acquisitions. The combination of the 4500 ICP-MS and the industry standard ChemStation software is already proven to be a powerful solution in many laboratories around the world. The semiquantitative analysis capability further increases the flexibility of the 4500 ICP-MS as a survey tool for screening samples, prior to full analysis.

element	mass	found	certified	unit
Li	7	32.8	31*	µg/g
Be	9	1600		ng/g
B	11	38.8		µg/g
Na	23	2400	2400	µg/g
Mg	24	9.2	11.3*	mg/g
Al	27	39.6	47*	mg/g
Si	29	6		mg/g
K	39	8.4	12.1*	mg/g
Ca	43	108	163*	mg/g
Sc	45	10.8	8.3	µg/g
Ti	47	3280	3000*	µg/g
V	51	64	66	µg/g
Cr	53	120	60	µg/g
Mn	55	560	631	µg/g
Fe	57	22.8	25.7*	mg/g
Co	59	10.4	8.9	µg/g
Ni	60	44	26*	µg/g
Cu	63	10	11	µg/g
Zn	66	96	104	µg/g
Ga	69	18	10*	µg/g
Ge	72	2200		ng/g
As	75	16.4	13.4	µg/g
Se	82	-	0.4*	ng/g
Br	79	8.4		µg/g

element	mass	found	certified	unit
Br	79	8.4		µg/g
Rb	85	60	51	µg/g
Sr	88	108	108	µg/g
Y	89	Internal Standard		mg/g
Zr	90	100		µg/g
Nb	93	12	12*	µg/g
Mo	95	2240	2500*	ng/g
Tc	99	-		ng/g
Ru	101	-		ng/g
Rh	103	-		ng/g
Pd	105	132		ng/g
Ag	107	440		ng/g
Cd	111	1560	1300*	ng/g
In	115	44		ng/g
Sn	118	2840		ng/g
Sb	121	1920	1700	ng/g
Te	125	-		ng/g
I	127	7.2		µg/g
Cs	133	6	5.4	µg/g
Ba	137	156	159	µg/g
La	139	38.8	28	µg/g
Ce	140	76	61	µg/g
Pr	141	8.8		µg/g
Nd	146	32	30	µg/g

element	mass	found	certified	unit
Sm	147	5.6	5.1	µg/g
Eu	153	1160	1000	ng/g
Gd	157	5.6		µg/g
Tb	159	720	600	ng/g
Dy	163	3280	3900	ng/g
Ho	165	720		ng/g
Er	166	2160		ng/g
Tm	169	248		ng/g
Yb	172	1860	2400	ng/g
Lu	175	228	300	ng/g
Hf	178	840		ng/g
Ta	181	760	800*	ng/g
W	182	1640		ng/g
Re	185	28.8		ng/g
Os	189	-		ng/g
Ir	193	-		ng/g
Pt	195	-		ng/g
Au	197	-		ng/g
Hg	202	-		ng/g
Tl	205	600		ng/g
Pb	208	68	60	mg/g
Bi	209	308		ng/g
Th	232	1160		ng/g
U	238	3000	2600	ng/g

**Table 2**

- Semiquantitative results from an analysis of IAEA Soil-7 standard.

Note that data marked with an asterisk are reference values, not certified

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